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<p>(54) Title: METALLOCENE COMPOUNDS, PROCESS FOR THEIR PREPRATION, AND THEIR USE IN CATALYSTS FOR THE POLYMERIZATION OF OLEFINS</p> <p>(57) Abstract</p> <p>A class of metallocene compounds having two cyclopentadienyl rings bridged by an alkylidene group is disclosed. These metallocene compounds can be suitably used as catalyst components for the polymerization of olefins. In particular, by polymerising propylene in the presence of a catalyst based on these metallocene compounds, polymers having very high isotactic indexes, high molecular weights and narrow molecular weight distributions can be obtained in high yields.</p>		

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TITLE:

METALLOCENE COMPOUNDS, PROCESS FOR THEIR PREPARATION, AND THEIR USE IN CATALYSTS FOR THE POLYMERIZATION OF OLEFINS

The present invention relates to a class of bridged metallocene compounds, to the process for their preparation and to the use of these metallocenes as catalyst components for the polymerization of olefins.

Metallocene compounds with two bridged cyclopentadienyl groups are known as catalyst components for the polymerization of olefins.

For example, European Patent Application EP-A-129,368 describes a catalyst system for the polymerization of olefins which comprises a bis-cyclopentadienyl coordination complex with a transition metal, wherein the two cyclopentadienyl groups can be joined by a bridging group.

In this type of metallocene compounds the two cyclopentadienyl groups are generally bridged by divalent radicals having two or more carbon atoms, such as an ethylidene group, or with atoms other than carbon, such as a dimethylsilanediyl group.

Metallocene compounds having two cyclopentadienyl groups bridged by a single carbon atom are also known. In particular, metallocene compounds of this type having two different cyclopentadienyl groups are known.

For example, European Patent Application EP-A-351,392 describes a catalyst which can be used for the preparation of syndiotactic polyolefins and contains a metallocene compound with two cyclopentadienyl groups linked by a bridge between them, in which one of the two cyclopentadienyl groups is substituted in a manner different from that of the other. The compound

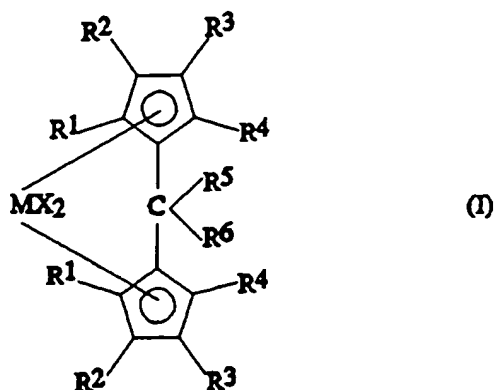
indicated as being preferred is isopropylidene-(fluorenyl)(cyclopentadienyl)hafnium dichloride.

As regards metallocene compounds having two equally substituted cyclopentadienyl groups bridged by a single carbon atom, in European Patent Application EP 416,566 it is described the polymerization of propylene, carried out in liquid monomer in the presence of a catalyst consisting of (A) an alumoxane and (B) a metallocene compound in which the cyclopentadienyl rings, which can be identical or different, are linked via a bridge of the formula $-R^5CR^6-$ in which R^5 and R^6 can have different meanings. The only compound given as an example is isopropylidene-bis(indenyl)zirconium dichloride. However, the thus obtainable propylene polymers have a very low molecular weight.

I.F.Urazowski et al. at the Xth Fechem Conference on Organometallic Chemistry held on September 5-10, 1993 in Agia Pelagia, Crete - Greece presented metallocene complexes of Ti and Zr obtained from two dicyclopentadienyl-dimethyl-methanes, namely those having an isopropyl or tertbutyl substituent on the 3-position of each cyclopentadienyl ring. However, only mechanisms of the formation of those complexes and their structural features on the basis of X-ray analysis were discussed.

A novel class of metallocene compounds has now been found which has two identical cyclopentadienyl ligands which are linked to one another by an alkylidene bridge and which can advantageously be used as catalyst components for the polymerization of olefins.

An object of the present invention is therefore a metallocene compound of the formula (I):



wherein R^1 , R^2 ,
 R^3 and R^4 ,
 which can be
 identical or

different, are hydrogen atoms or C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl groups which can contain silicon or germanium atoms, R^3 being different from R^2 and from a hydrogen atom, and wherein R^1 and R^2 on the same cyclopentadienyl ring can form a ring having 5 to 8 carbon atoms;

R^5 is a hydrogen atom or a $-CHR^7R^8$ group;

R^6 is a C_6 - C_{20} -aryl radical or a $-CHR^9R^{10}$ group;

R^5 and R^6 can form a ring having 3 to 8 carbon atoms which can contain hetero atoms;

R^7 , R^8 , R^9 and R^{10} , which can be identical or different, are hydrogen atoms or C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radicals which can contain hetero atoms such as nitrogen, phosphor, oxygen or sulphur, and two R^7 , R^8 , R^9 and R^{10} substituents can form a ring having 3 to 8 carbon atoms which can contain hetero atoms;

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements (new IUPAC version);

the X substituents, which can be identical or different, are hydrogen atoms, halogen atoms or R, OR, SR, NR_2 or PR_2 groups,

wherein the R substituents are C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals which can contain silicon or germanium atoms; with the proviso that, when the R¹, R² and R⁴ substituents are hydrogen atoms and the R⁵ and the R⁶ substituents are methyl groups, then the R³ substituents are other than an isopropyl or tertbutyl group.

The transition metal M is preferably selected from titanium, zirconium and hafnium and, more preferably, is zirconium.

The X substituents are preferably chlorine atoms or methyl radicals.

A particularly interesting class of metallocenes according to the invention is that of the compounds of the formula (I) in which the R² substituents are hydrogen atoms. The R¹ substituents are preferably different from hydrogen atoms. The R³ substituents are preferably carbon, silicon or germanium atoms substituted with three alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl groups having 1 to 10 carbon atoms. The R⁴ substituents are preferably hydrogen atoms. Non-limiting examples of metallocene compounds belonging to this class are:

isopropylidene-bis(3-methyl-cyclopentadienyl)zirconium dichloride,

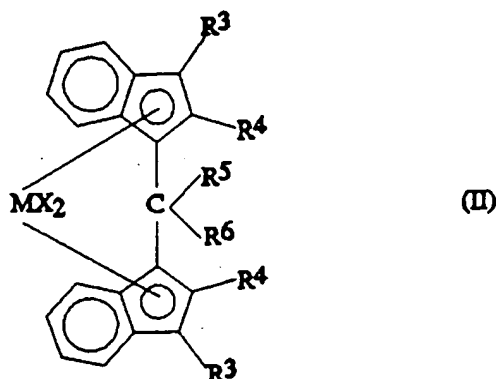
isopropylidene-bis(3-isopropyl-cyclopentadienyl)zirconium dichloride,

isopropylidene-bis(3-t-butyl-cyclopentadienyl)zirconium dichloride,

isopropylidene-bis(2,4-dimethyl-cyclopentadienyl)zirconium dichloride,

isopropylidene-bis(2-methyl-4-t-butyl-cyclopentadienyl)zirconium dichloride and
isopropylidene-bis(2-methyl-4-phenyl-cyclopentadienyl)zirconium dichloride.

Another particularly interesting class of metallocenes according to the invention is that of the compounds of the formula (II):



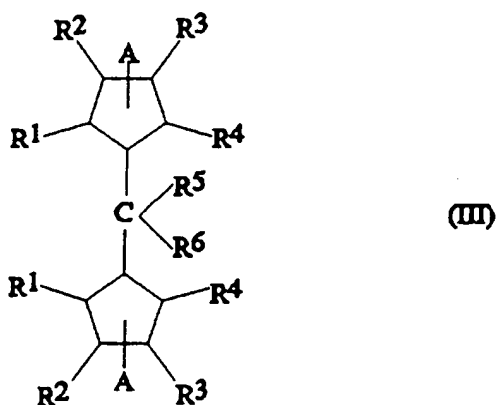
and the corresponding bis-4,5,6,7-tetrahydroindenyl compounds, wherein R^3 , R^4 , R^5 , R^6 , M and X are defined as above, and the six-carbon-atom rings of the indenyl ligands can optionally be substituted. The R^3 substituents are preferably carbon, silicon or germanium atoms substituted with three alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl groups having 1 to 10 carbon atoms. The R^4 substituents are preferably hydrogen atoms. Non-limiting examples of metallocene compounds belonging to this class are:
isopropylidene-bis(3-methyl-indenyl)zirconium dichloride,
isopropylidene-bis(3-ethyl-indenyl)zirconium dichloride,
isopropylidene-bis(3-isopropyl-indenyl)zirconium dichloride,
isopropylidene-bis(3-t-butyl-indenyl)zirconium dichloride,

isopropylidene-bis(3-trimethylsilyl-indenyl)zirconium dichloride,

isopropylidene-bis(3-trimethylgermyl-indenyl)zirconium dichloride,

isopropylidene-bis(3-t-butyl-4,5,6,7-tetrahydroindenyl) zirconium dichloride.

The metallocene compounds of the formula (I) can be prepared by a process which represents another object of the present invention and which comprises the reaction of the corresponding bis-cyclopentadienyl ligands of the formula (III):



wherein R^1 , R^2 ,

R^3 , R^4 , R^5 and

R^6 are defined as above, and A is a suitable leaving group, with a compound of the formula MX_4 , wherein M and X are defined as above. The double bonds of the cyclopentadienyl rings in the ligands of formula (III) can be in any of the allowed positions. The ligands of the formula (III) can be prepared, for example, by the method described in the co-pending Italian Patent Application No. MI/95A/100 in the name of the same Applicant.

In the case in which at least one substituent X in the metallocene compound of the formula (I) which is to be prepared is other than a halogen, it is necessary to substitute at least one

substituent X in the metallocene obtained by at least one substituent X other than a halogen.

The reaction of substituting substituents X by substituents X other than a halogen is carried out using generally applied methods. For example, if the desired substituents X are alkyl groups, the metallocenes can be made to react with alkylmagnesium halides (Grignard reagents) or with alkyllithium compounds.

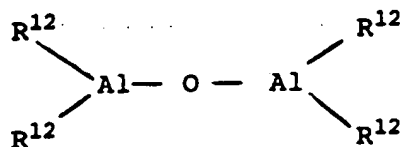
The metallocene compounds of the present invention can conveniently be used as catalyst components for the polymerization of olefins.

Still another object of the present invention is therefore a catalyst for the polymerization of olefins, consisting of the product of the reaction between:

- (a) a metallocene compound according to the invention, and
- (b) an alumoxane or a compound able to form an alkylmetallocene cation.

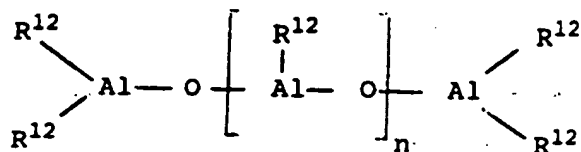
In the catalyst used in the process according to the invention, both the metallocene compound of the formula (I) and the alumoxane can be present as the product of the reaction with an organometallic aluminium compound of the formula AlR^{11}_3 or $Al_2R^{11}_6$, in which the substituents R^{11} which can be identical or different are defined as for the substituents R or are halogen atoms.

The alumoxane used in the catalyst according to the invention is a linear, branched or cyclic compound containing at least one group of the type:

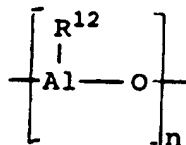


wherein the substituents R^{12} which can be identical or different are defined as for the substituent R or are a group $-O-Al(R^{12})_2$ and, if appropriate, some R^{12} can be halogen atoms.

In particular, alumoxanes of the formula:



can be used in the case of linear compounds, wherein n is 0 or an integer of between 1 and 40 and the substituents R^{12} are defined as for the substituents R, or alumoxanes of the formula:



can be used in the case of cyclic compounds, with n being an integer of between 2 and 40 and the substituents R^{12} being defined as for the substituents R.

The substituents R^{12} are preferably methyl, ethyl, isobutyl or 2,4,4-trimethyl-pentyl.

Examples of alumoxanes suitable for use according to the present invention are methylalumoxane (MAO), isobutylalumoxane (TIBAO) and 2,4,4-trimethyl-pentylalumoxane (TIOAO).

Non-limiting examples of aluminium compounds of the formula AlR^{11}_3 or $Al_2R^{11}_6$ are:

$Al(Me)_3$, $Al(Et)_3$, $AlH(Et)_2$, $Al(iBu)_3$, $AlH(iBu)_2$, $Al(iHex)_3$, $Al(iOct)_3$, $Al(C_6H_5)_3$, $Al(CH_2C_6H_5)_3$, $Al(CH_2CMe_3)_3$, $Al(CH_2SiMe_3)_3$, $Al(Me)_2iBu$, $Al(Me)_2Et$, $AlMe(Et)_2$, $AlMe(iBu)_2$, $Al(Me)_2iBu$, $Al(Me)_2Cl$, $Al(Et)_2Cl$, $AlEtCl_2$ and $Al_2(Et)_3Cl_3$, wherein Me = methyl, Et = ethyl, iBu = isobutyl and iHex = isohexyl, iOct = 2,4,4-trimethyl-pentyl.

Amongst the above aluminium compounds, trimethylaluminium (TMA) and triisobutylaluminium (TIBAL) are preferred.

Non-limiting examples of compounds able to form an alkylmetallocene cation are compounds of the formula Y^+Z^- , wherein Y^+ is a Brönsted acid, able to donate a proton and to react irreversibly with a substituent X of the compound of the formula (I), and Z^- is a compatible anion which does not coordinate and which is able to stabilize the active catalytic species which results from the reaction of the two compounds and which is sufficiently labile to be displaceable by an olefin substrate. Preferably, the anion Z^- consists of one or more boron atoms. More preferably, the anion Z^- is an anion of the formula $BAR_4^{(-)}$, wherein the substituents Ar which can be identical or different are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred. Moreover, compounds of the formula BAR_3 can conveniently be used.

The catalysts of the present invention can also be used on inert supports. This is achieved by depositing the metallocene compound (A) or the product of the reaction thereof with the component (B), or the component (B) and then the metallocene compound (A) on inert supports such as, for example, silica, alumina, styrene/divinylbenzene copolymers or polyethylene.

The solid compound thus obtained, in combination with the further addition of the alkylaluminium compound either as such or prereacted with water if necessary, is usefully employed in gas-phase polymerization.

A further object of the present invention is a process for the polymerization of olefins, which comprises the polymeriza-

tion reaction of one or more olefin monomers in the presence of a catalyst as described above.

Preferred olefin monomers are ethylene, the α -olefins and the cycloolefins. The catalysts according to the invention can conveniently be used, for instance, in the homopolymerization reactions of ethylene or of α -olefins such as propylene and 1-butene, in the copolymerization reactions of ethylene with α -olefins such as propylene and 1-butene, and also in the copolymerization reactions of propylene with C_4 - C_{10} α -olefins such as 1-butene. Particularly interesting results are achieved when the catalysts of the invention are used for the polymerization of propylene.

Thus, according to an embodiment of the process for olefin polymerization of the invention, propylene is polymerized in the presence of a metallocene compound of the formula (II), wherein the R^3 substituents are carbon, silicon or germanium atoms substituted with three alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl groups having 1 to 10 carbon atoms, and wherein R^4 , R^5 , R^6 , M and X are defined as above. The R^4 substituents are preferably hydrogen atoms. Examples of those metallocene compounds are:

isopropylidene-bis(3-t-butyl-indenyl)zirconium dichloride,
isopropylidene-bis(3-trimethylsilyl-indenyl)zirconium dichloride, and
isopropylidene-bis(3-trimethylgermyl-indenyl)zirconium dichloride.

The thus obtainable propylene polymers have narrow molecular weight distributions coupled with high isotactic indexes and a very high levels of regioregularity. In fact, the ^{13}C -NMR analysis carried out on these polymers does not show structural

units due to regioirregular insertions. Reference is made to "Macromolecules, 1995, vol.28, pagg. 6667-6676".

Thus, another object of the present invention is a propylene homopolymer having the following characteristics:

- molecular weight distribution (Mw/Mn) lower than 4, preferably lower than 3.5, more preferably lower than 3,
- isotactic (mmmm) pentads, as determined by ^{13}C -NMR analyses, higher than 70%, preferably comprised between 75 and 97%, more preferably between 80 and 95%,
- no structural units due to regioirregular insertions detectable at the ^{13}C -NMR analysis carried out with a 300 MHz instrument.

If the polymerization of propylene is carried out in the presence of a bis-4,5,6,7-tetrahydroindenyl metallocene compound corresponding to the above said compounds of the formula (II), a very low molecular weight polypropylene wax is obtained. Notwithstanding the low molecular weight, these waxes have fairly high isotactic indexes as demonstrated by the presence of a melting point and by the values of isotactic (m) diads, as determined by ^{13}C -NMR analyses, which are generally higher than 90%.

According to another embodiment of the process for olefin polymerization of the invention, propylene is polymerized in the presence of a metallocene compound of the formula (I) in which the R^2 substituents are hydrogen atoms and the R^3 substituents are carbon, silicon or germanium atoms substituted with three alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl groups having 1 to 10 carbon atoms. The R^4 substituents are preferably hydrogen atoms. Examples of those metallocene compounds are:

isopropylidene-bis(3-t-butyl-cyclopentadienyl)zirconium dichloride, and

isopropylidene-bis(2-methyl-4-t-butyl-cyclopentadienyl)zirconium dichloride.

The thus obtainable propylene polymers, besides narrow molecular weight distributions, have very high isotactic indexes, as results from their high melting points which are generally higher than 155°C and also higher than 160°C.

Thus, a further object of the present invention is a propylene homopolymer having the following characteristics:

- molecular weight distribution (Mw/Mn) lower than 4, preferably lower than 3.5, more preferably lower than 3,
- isotactic (m) diads, as determined by ^{13}C -NMR analyses, higher than 99%, preferably higher than 99.5%.

Even the values of isotactic (mmmm) pentads for these polymers can be as high as 99% and over.

These polymers do not have a very high level of regioregularity. In fact, the ^{13}C -NMR analysis carried out with a 300 MHz instrument on these polymers generally shows the presence of a low amount of structural units due to regioirregular insertions, such as 1,3 insertions.

Particularly interesting results are achieved when in the above said specific metallocene compounds of the formula (I) the R^1 substituents are different from hydrogen atoms, such as for the isopropylidene-bis(2-methyl-4-t-butyl-cyclopentadienyl)zirconium dichloride. It is thus possible to obtain propylene polymers having very high isotactic indexes, as results from their melting points which can be higher than 160°C even at polymeri-

zation temperatures of industrial interest, such as 50°C and higher.

The propylene polymers obtainable from the process of the invention have low xylene-soluble fractions, generally lower than 5% by weight, preferably lower than 3% by weight, more preferably lower than 1% by weight.

The polymerization reaction of propylene according to the invention can be carried out in the presence of a C₄-C₁₀ α-olefin comonomer, such as 1-butene. It is thus possible to obtain propylene copolymers with 0.1-10% by moles of a C₄-C₁₀ α-olefin comonomer having characteristics similar to those of the corresponding homopolymer but a lower melting point. Notwithstanding the presence of a comonomer, these copolymers still have an extremely low xylene-soluble fractions, generally lower than 3% by weight, preferably lower than 2% by weight, more preferably lower than 1% by weight.

Thus, a still further object of the present invention is a propylene copolymers with 0.1-10% by moles of a C₄-C₁₀ α-olefin comonomer, preferably 1-butene, having the following characteristics:

- isotactic (m) diads, as determined by ¹³C-NMR analyses, higher than 70%, preferably higher than 75%, more preferably higher than 80%,
- molecular weight distribution (Mw/Mn) lower than 4, preferably lower than 3.5, more preferably lower than 3,
- xylene-soluble fractions lower than 3% by weight, preferably lower than 2% by weight, more preferably lower than 1% by weight.

The process for the polymerization of olefins according to the invention can be carried out in the liquid phase in the presence or absence of an inert hydrocarbon solvent, or in the gas

phase. The hydrocarbon solvent can either be aromatic such as toluene, or aliphatic such as propane, hexane, heptane, isobutane or cyclohexane.

The polymerization temperature is generally comprised between -100°C and $+80^{\circ}\text{C}$, and more particularly between -50°C and $+50^{\circ}\text{C}$. The lower the polymerization temperature, the higher are the resulting molecular weights of the polymers obtained.

The molecular weight of the polymers can be also varied by varying the type or the concentration of the catalyst components or using molecular weight regulators such as, for example, hydrogen.

The molecular weight distribution can be varied by using mixtures of different metallocene compounds or by carrying out the polymerization in several stages at different polymerization temperatures and/or different concentrations of the molecular weight regulators.

The polymerization yields depend on the purity of the metallocene compound of the catalyst. The metallocene compounds obtained by the process of the invention can therefore be used as such or can be subjected to purification treatments.

The components of the catalyst can be put into contact with one another before the polymerization. The contact time is generally between 1 and 60 minutes, preferably between 5 and 20 minutes. The pre-contact concentrations are between 10^{-2} and 10^{-8} mol/l for the metallocene component (A), while they are between 10^{-2} and 10^{-3} mol/l for the component (B). The pre-contact is generally effected in the presence of a hydrocarbon solvent and, if appropriate, of small quantities of monomer.

The following examples are given for illustrative purposes and do not limit the invention.

CHARACTERIZATIONS

The ^1H -NMR analyses were carried out on a Bruker 200 MHz instrument with a pulse amplitude of 40° and a 1 second interval between pulses. 128 to 512 data points were accumulated for each sample, depending on the solubility of the various compounds.

The ^{13}C -NMR analyses were carried out on a Varian UNITY-300 instrument operating at 75.4 MHz. The samples were analyzed in a 15% solution in deuterioethane tetrachloride at 130°C . For each sample, 6000 data points were accumulated with an interval of 12 seconds between each pulse.

The intrinsic viscosity (η) is measured in tetralin at 135°C .

Measures of Differential Scanning Calorimetry (D.S.C.) were carried out on an instrument DSC-7 of Perkin Elmer Co. Ltd., according to the following method. About 10 mg of sample obtained from the polymerization were cooled to -25°C and thereafter heated at 200°C with a scanning speed corresponding to $10^\circ\text{C}/\text{minute}$. The sample was kept at 200°C for 5 minutes and thereafter cooled with a scanning speed corresponding to $10^\circ\text{C}/\text{minute}$. Then, a second scanning was carried out according to the same modalities of the first one. The values reported are those obtained in the first scanning.

The distribution of molecular weights was determined by GPC carried out on an instrument WATERS 150 in orthodichlorobenzene at 135°C .

The solubility in xylene of the propylene polymers is determined by dissolving 2 g of polymer in 250 ml of xylene at 135°C and stirring the system. After 20 minutes, the solution is cooled down to 25°C . After 30 minutes the precipitated material is filtered; the solution is evaporated in nitrogen flow and the

residue is dried at 80°C. In this way the percentage of polymer soluble in xylene at room temperature (XSRT) is calculated and thus also the percentage of insoluble polymer.

PREPARATION OF THE METALLOCENES

All the operations were carried out in a dry nitrogen atmosphere, using the conventional techniques for the handling of compounds which are sensitive to air.

THF = tetrahydrofuran

Et₂O = ethyl ether

DME = dimethoxyethane

EXAMPLE 1

rac-isopropylidene-bis(3-trimethylsilyl-indenyl)zirconium dichloride

(a) Synthesis of 2,2-bis(indenyl)propane

23.5 ml (200 mmol) of indene was added within 0.5 hours to a suspension of 15 g of milled KOH in 150 ml of DME. The mixture was heated to reflux. Then 7.5 ml (100 mmol) of acetone was added dropwise within 0.5 hours and the mixture was stirred under reflux for additional 2 hours. The resulting mixture was cooled, treated with 200 ml of diluted phosphoric acid until neutralization and then with 100 ml of diethyl ether. The organic layer was separated, washed with water and dried over Na₂SO₄. Then the solvent was removed in vacuo and the residue was distilled at 130-160°C and 0.01 torr. The broad fraction was collected and recrystallized from a 1:1 ether/hexane mixture, thus obtaining 20.4 g of the product (yield 72%). ¹H-NMR (acetone-d₆, 30°C) δ: 7.37 (d, 2H); 7.32 (d, 2H); 6.98 (m, 4H); 6.60 (t, 2H) (=CH-) 3.38 (d, 4H, -CH₂-) 1.74 (s, 6H, -CH₃).

(b) Synthesis of 2,2-bis(3-trimethylsilyl-indenyl)propane

5.45 g (20 mmol) of 2,2-bis(indenyl)propane was dissolved in 100 ml of ether. The solution thus obtained was taken to -20°C , and 22 ml of a 2.0 M solution of n-butyl-lithium in pentane was added, thus giving a suspension of dilithium-2,2-bis(indenyl)propane. 8.77 g (30.85 mmol) of dilithium 2,2-bis(indenyl)propane was dissolved in 100 ml of ether, and 10 ml of Me_3SiCl (excess) was added at a temperature of -40°C . The resulting mixture was allowed to return to room temperature. The organic phase was then separated off, the solvent removed and the product dried in vacuo.

(c) Synthesis of rac-isopropylidene-bis(3-trimethylsilyl-indenyl)zirconium dichloride

8.34 g (20 mmol) of 2,2-bis(3-trimethylsilyl-indenyl)propane were dissolved in 100 ml of ether. The solution thus obtained was taken to -20°C , and 22 ml of a 2.0 M solution of n-butyl-lithium in pentane were added, a suspension of the dilithium 2,2-bis(3-trimethylsilyl-indenyl)propane thus being obtained. To this suspension, which was first allowed to rise to room temperature and was then cooled to -40°C , 12.06 g (50 mmol) of triethylstannylchloride were added. The organic layer was separated off and subjected to evaporation, and 50 ml of toluene were then added. Subsequently, 4.66 g (20 mmol) of ZrCl_4 was added, and the mixture thus obtained was taken to 80°C and stirred for a further 6 hours. The toluene was then removed, and the product was washed with DME (5 x 50 ml) and recrystallized from DME. 3.69 g of pure rac-isopropylidene-bis(3-trimethylsilyl-indenyl)zirconium dichloride was obtained (yield 32%). $^1\text{H-NMR}$ (CD_2Cl_2 , 30°C) δ : 7.80 (d, 2H); 7.55 (d, 2H); 7.30 (t, 2H); 7.06 (t, 2H); 6.06 (s, 2H); 2.38 (s, 6H); 0.23 (s, 18H).

EXAMPLE 2

rac-isopropylidene-bis(3-methyl-indenyl)zirconium dichloride(a) Synthesis of 2,2-bis(3-methyl-indenyl)propane

It was worked according to the procedure described at point (a) of example 1 except that, instead of indene, 200 mmol of 3-methyl-indene was used and that, after the acetone addition, the mixture was stirred under reflux for 3 hours. The temperature of distillation was 135-165°C. The product was isolated as dilithium salt (yield 65%). ¹H-NMR (THF-d₈, 30°C) δ: 7.42 ("d", 2H); 7.10 ("d", 2H); 6.26 ("t", 2H); 6.18 ("t", 2H) {ABCD, J=9Hz} 6.47 (s, 2H); 2.33 (s, 6H, Ind-CH₃); 1.90 (s, 6H, >CMe₂).

(b) Synthesis of rac-isopropylidene-bis(3-methyl-indenyl)zirconium dichloride

It was worked according to the procedure described at point (c) of example 1 except that, instead of 2,2-bis(3-trimethylsilyl-indenyl)propane, 20 mmol of the dilithium salt of 2,2-bis(3-methyl-indenyl)propane was used, and that the product was recrystallized from toluene. Pure rac-isopropylidene-bis(3-methyl-indenyl)zirconium dichloride was obtained. ¹H-NMR (CD₂Cl₂, 30°C) δ: 7.64 (d, 2H); 7.42 (d, 2H); 7.22 (m, 2H); 6.96 (m, 2H); 5.83 (s, 2H); 2.30 (s, 6H); 2.28 (s, 6H).

EXAMPLE 3rac-isopropylidene-bis(3-isopropyl-indenyl)zirconium dichloride(a) Synthesis of 2,2-bis(3-isopropyl-indenyl)propane

It was worked according to the procedure described at point (a) of example 1 except that, instead of indene, 200 mmol of 3-isopropyl-indene was used and that, after the acetone addition, the mixture was stirred under reflux for 4 hours. The temperature of distillation was 140-175°C. The product was isolated as dilithium salt (yield 63%). ¹H-NMR (THF-d₈, 30°C) δ: 7.45 ("d", 2H) 7.27 ("d", 2H) 6.30 ("t", 2H) 6.23 ("t", 2H) {ABCD,

J=8.0Hz} 6.63 (s,2H) 3.30 (sept, J=7.0Hz,2H, -CH(CH₃)₂); 1.98 (s, 6H, >CMe₂) 1.35 (d, J=7.0Hz, 12H, -CH(CH₃)₂).

(b) Synthesis of rac-isopropylidene-bis(3-isopropyl-indenyl) zirconium dichloride

It was worked according to the procedure described at point (c) of example 1 except that, instead of 2,2-bis(3-trimethylsilyl-indenyl)propane, 20 mmol of the dilithium salt of 2,2-bis(3-isopropyl-indenyl)propane was used, and that the product was recrystallized from DME. Pure rac-isopropylidene-bis(3-isopropyl-indenyl)zirconium dichloride was obtained. ¹H-NMR (toluene-d₈, 30°C) δ: 7.34 (m,4H); 6.98 (m,2H); 6.69 (m,2H); 5.78 (s,2H); 3.14 (sept,2H); 1.81 (s,6H); 1.20 (d,12H).

EXAMPLE 4

rac-isopropylidene-bis(3-t-butyl-indenyl)zirconium dichloride

(a) Synthesis of 2,2-bis(3-tertbutyl-indenyl)propane

It was worked according to the procedure described at point (a) of example 1 except that, instead of indene, 200 mmol of 3-tertbutyl-indene was used and that, after the acetone addition, the mixture was stirred under reflux for 4 hours. The temperature of distillation was 145-185°C. The product was isolated as dilithium salt (yield 48%). ¹H-NMR (THF-d₈, 30°C) δ: 8.17 ("t",4H) 6.95 (mm,4K) {ABCD} 7.36 (s,2H) 2.70 (s,6H,>CMe₂) 2.19 (s, 18H, -CMe₃).

(b) Synthesis of rac-isopropylidene-bis(3-tertbutyl-indenyl)zirconium dichloride

It was worked according to the procedure described at point (c) of example 1 except that, instead of 2,2-bis(3-trimethylsilyl-indenyl)propane, 20 mmol of the dilithium salt of 2,2-bis(3-tertbutyl-indenyl)propane was used, and that the product was recrystallized from DME. Pure rac-isopropylidene-

bis(3-tertbutyl-indenyl)zirconium dichloride was obtained. ^1H -NMR (CD_2Cl_2 , 30°C) δ : 7.75 (m, 4H); 7.25 (dd, 2H); 6.97 (dd, 2H); 5.97 (s, 2H); 2.33 (s, 6H); 1.37 (s, 18H).

EXAMPLE 5

rac-isopropylidene-bis(3-t-butyl-4,5,6,7-tetrahydro-indenyl) zirconium dichloride

In a 100 ml glass-autoclave were introduced 0.66 g of rac-isopropylidene-bis(3-t-butyl-indenyl)zirconium dichloride, 40 mg of PtO_2 and 50 ml of CH_2Cl_2 . 5 atm of H_2 were pressurized in and the mixture was stirred for 4 hours at room temperature. The mixture was filtered, the filtrate brought to dryness and 0.56 g of a yellow solid was isolated, which was further purified by washing with hexane and Et_2O . 0.22 g of a yellow powder were thus obtained. ^1H -NMR (CDCl_3): 5.3(s), 2.6-2.9(m), 2.2-2.4(m), 1.85(s), 1.4-1.8(m), 1.3(s).

EXAMPLE 6

rac-isopropylidene-bis(3-t-butyl-cyclopentadienyl)zirconium dichloride

(a) Synthesis of 2,2-bis(3-t-butyl-cyclopentadienyl)propane

10 g of KOH, 150 mmol of t-butyl-cyclopentadiene and 4.35 g of acetone were suspended in 100 ml of DME and the mixture obtained was heated to reflux and stirred for 2 hours. The mixture was then cooled and treated with 200 ml of water and 100 ml of diethyl ether. The organic phase was separated off, washed with water and dried over CaCl_2 . The solvent was then evaporated in vacuo and the residue was distilled at a temperature of $145-165^\circ\text{C}$. The broad fraction was collected and recrystallized (yield 81%). ^1H -NMR (CDCl_3) δ : 6.3-5.7 (m, 4H) 3.0-2.8 (m, 4H) 1.5-1.4 (m, 6H) 1.3-1.2 (m, 18H).

(b) Synthesis of rac-isopropylidene-bis(3-t-butyl-cyclopentadienyl)zirconium dichloride

It was worked according to the procedure described at point (c) of example 1 except that, instead of 2,2-bis(3-trimethylsilyl-indenyl)propane, 6.01 g (20 mmol) of 2,2-bis(3-t-butyl-cyclopentadienyl)propane, and that the product was washed with 50 ml of pentane and then recrystallized from ether. 1.97 g of pure rac-isopropylidene-bis(3-t-butyl-cyclopentadienyl)zirconium dichloride was obtained (yield 22%). ¹H-NMR (THF-d₈, 30°C) δ: 5.65 (t, 2H); 5.53 (t, 2H); 1.60 (s, 6H); 1.23 (s, 8H).

EXAMPLE 7

Isopropylidene-bis(2-methyl-4-t-butyl-cyclopentadienyl) zirconium dichloride

(a) Synthesis of 2,2-bis(2-methyl-4-t-butyl-cyclopentadienyl)propane

17.8 g (131 mmol) of 2-methyl-4-t-butyl-cyclopentadiene was added within 0.5 hours under vigorous stirring to a suspension of 10 g of KOH powder in 100 ml of DME. The obtained mixture was heated to reflux. Then 4.8 ml (66 mmol) of acetone was added dropwise within 0.5 hours and the mixture was stirred under reflux for additional 6 hours. The resulting mixture was cooled, treated with 200 ml of diluted phosphoric acid until neutralization and then with 100 ml of diethyl ether. The organic layer was separated, washed with water and dried over Na₂SO₄. Then the solvent was removed in vacuo and the residue was distilled under 0.01 torr. The 130-160°C broad fraction was collected, diluted with 30 ml of Et₂O and treated with 60 ml of a 2.0M solution of n-butyllithium in hexane. White crystalline precipitate of the product was isolated, washed twice by 20 ml of Et₂O and dried

in vacuo (yield 60%). $^1\text{H-NMR}$ (THF-d_8 , 30°C) δ : 5.52 ("d", 2H); 5.22 ("d", 2H); 3.58 (s, 6H); 1.58 (s, 6H); 1.18 (s, 18H).

(b) Synthesis of isopropylidene-bis(2-methyl-4-*t*-butyl-cyclopentadienyl)zirconium dichloride

3.24 g (10 mmol) of the product obtained in step (a) was treated with 3.98 g (20 mmol) of trimethylstannylchloride diluted in 50 ml of Et_2O . The solution was decanted from LiCl precipitate, the solvent was removed and the residue was diluted with 40 ml of toluene. The resulting solution was treated with 2.33 g (10 mmol) of ZrCl_4 and the mixture was stirred until the ZrCl_4 was dissolved. Then the solvent was removed and the residual solid was recrystallized from heptane. A 1:1 *rac*-/*meso*- mixture of isopropylidene-bis(2-methyl-4-*t*-butyl-cyclopentadienyl)zirconium dichloride was obtained (yield 87%). Recrystallization from DME yields a 2:1 *rac*-/*meso*- mixture. $^1\text{H-NMR}$ (CD_2Cl_2 ; 30°C) *rac*-form δ : 6.29 (d, $J=3.0\text{Hz}$, 2H); 5.51 (d, $J=3.0\text{Hz}$, 2H) [cyclopentadienyl ring]; 2.16 (s, 6H, $-\text{CH}_3$ in ring); 1.91 (s, 6H, $>\text{C}(\text{CH}_3)_2$); 1.28 (s, 18H, $-\text{C}(\text{CH}_3)_3$). *meso*-form δ : 6.08 (d, $J=3.0\text{Hz}$, 2H); 5.65 (d, 2H) [cyclopentadienyl ring]; 2.29 (s, 6H, $-\text{CH}_3$ in ring); 2.01, 1.88 (s, 2x3H, $>\text{C}(\text{CH}_3)_2$); 1.23 (s, 18H, $-\text{C}(\text{CH}_3)_3$). $^{13}\text{C-NMR}$ ("") δ : 145.5; 118.2 [quat. C in ring]; 120.7; 106.2; 100.2 [tert. C in ring]; 37.0; 33.0; [$>\text{C}<$]; 30.1 [$\text{C}(\text{CH}_3)_3$]; 24.2 [$>\text{C}(\text{CH}_3)_2$].

EXAMPLE 8

pseudorac-benzilidene-bis(indenyl)zirconium dichloride

(a) Synthesis of bis(indenyl)phenylmethane

It was worked according to the procedure described at point (a) of example 1 except that, instead of acetone, 100 mmol of benzaldehyde was used and that, after the benzaldehyde addition, the mixture was stirred under reflux for 5 hours. The temperatu-

re of distillation was 140-170°C. The collected fraction was recrystallized from a heptane (yield 60%). $^1\text{H-NMR}$ (acetone- d_6 , 30°C) δ : 7.52-7.18 {m, 13H,} 6.05 (q, 2H, =CH-) 5.39 (m, 1H, >CH-) 3.40 (br.s., 4H, -CH₂-). $^{13}\text{C-NMR}$ (CD₂Cl₂, 30°C) δ 145.6; 145.1; 141.5 (=C<) 131.8; 129.3; 128.7; 127.0; 126.2; 124.1; 120.2 (=CH-) 44.5 (>CH-) 38.1 (-CH₂-).

(b) Synthesis of pseudorac-benzilidene-bis(indenyl)zirconium dichloride

It was worked according to the procedure described at point (c) of example 1 except that, instead of 2,2-bis(3-trimethylsilyl-indenyl)propane, 20 mmol of the dilithium salt of bis(indenyl)phenylmethane was used, and that the product was recrystallized from DME. pseudorac-benzilidene-bis(indenyl)zirconium dichloride was obtained (due to unsimmetry of the bridge, the anti- isomer can not be the exact rac- isomer). $^1\text{H-NMR}$ (CD₂Cl₂, 30°C) δ : 7.84-7.12 (groups of multiplets, 12H); 6.76 (t, 1H); 6.70 (d, 1H); 6.60 (d, 1H); 6.11 (two doublets, 1H+1H); 6.51 (br.s, 1H).

POLYMERIZATION OF PROPYLENE

MODIFIED METHYLALUMOXANE (M-MAO)

A commercial product (ALBEMARLE) was used as such in a Isopar C solution (62 g of Al/l).

EXAMPLES 9-10

A 1 l steel autoclave, equipped with a jacket, a stirrer system and a resistance heater connected to a thermostat for temperature control, and cleaned beforehand with a solution of Al_iBu₃ in hexane and then dried at 60°C under a nitrogen stream, was charged with 0.4 l of propylene. The autoclave is then brought to the desired temperature, and 2.25 ml of a solution of M-MAO in Isopar C and 0.5 ml of toluene containing 1 mg of the

metallocene of Example 1, aged for 10 minutes, are added thereto. The polymerization is carried out for 1 hour. The polymerization conditions and the data relating to the characterization of the obtained polymers are indicated in Table 1.

EXAMPLES 11-17

The procedure followed was as described in Examples 9-10, using a 2.3 l steel autoclave, equipped with a jacket, stirrer and resistance heater, and connected to a thermostat for temperature control. The polymerization conditions and the data relating to the characterization of the obtained polymers are indicated in Table 1.

EXAMPLES 18-22

The procedure followed was as described in Examples 9-10, except that the metallocene of Example 4 was used. The polymerization conditions and the data relating to the characterization of the obtained polymers are indicated in Table 1.

EXAMPLES 23-25

The procedure followed was as described in Examples 18-22, except that the metallocene of Example 4 was used as a 7:3 rac-/meso mixture obtained before recrystallization. The polymerization conditions and the data relating to the characterization of the obtained polymers are indicated in Table 1.

EXAMPLES 26-27

The procedure followed was as described in Examples 9-10, except that the metallocene of Example 5 was used. The polymerization conditions and the data relating to the characterization of the obtained polymers are indicated in Table 1.

EXAMPLE 28

The procedure followed was as described in Examples 9-10, using 1 mg of the metallocene of Example 6. The polymerization

conditions and the data relating to the characterization of the obtained polymers are indicated in Table 1.

EXAMPLE 29

The procedure followed was as described in Examples 11-17, using 1 mg of the metallocene of Example 6. The polymerization conditions and the data relating to the characterization of the obtained polymers are indicated in Table 1.

EXAMPLES 30-34

The procedure followed was as described in Examples 9-10, except that the metallocene of Example 7 was used. The polymerization conditions and the data relating to the characterization of the obtained polymers are indicated in Table 1.

EXAMPLES 35-36

The procedure followed was as described in Examples 30-34, except that a 100 litres autoclave was used. The polymerization conditions and the data relating to the characterization of the obtained polymers are indicated in Table 1.

EXAMPLES 37-38

The procedure followed was as described in Examples 9-10, except that 235 g (0.45 l) of propylene and 28 g of 1-butene were charged into the autoclave.

The metallocene used, the polymerization conditions and the data relating to the characterization of the obtained copolymers are indicated in Table 2.

TABLE 1

Ex	metallocene	Zr (μ mol)	Al/Zr (mol)	T (°C)	yield (g)	activity ($\text{Kg}_{\text{poly}}/\text{mmol}_{\text{Zr}}\text{h}$)	I.V. (dL/g)	Mw/Mn	XSRT (%w)	T _m (°C)	ΔH_m (J/g)	m (%)	mmmm (%)	2,1 insertion %
9	$\text{Me}_2\text{C}(\text{3-TMS-Ind})_2\text{ZrCl}_2$	1.72	1500	70	45.0	26.2	0.53			126	65	92.82	82.70	0
10	"	1.73	3000	50	66.1	38.1	0.78			140	77	94.81	87.36	0
11	"	6.93	3000	40	98.4	14.2	0.77			139	76	95.94	90.06	0
12	"	6.93	3000	30	49.4	7.1	0.98		<1	142	73	96.55	91.51	0
13	"	10.40	3000	20	93.6	9.0	1.04			144	82	97.23	93.18	0
14	"	10.40	500	20	10.6	1.0	1.27			146	77			
15	"	10.40	1000	20	24.2	2.3	1.35			145	78			
16	"	10.40	1500	20	66.8	6.4	1.22			145	81			
17	"	3.47	10000	20	23.3	6.7	1.05			146	68			
18	$\text{Me}_2\text{C}(\text{3-t-Bu-Ind})_2\text{ZrCl}_2$	0.18	8000	70	20.2	109.9	0.33			140	88	95.50	89	0
19	"	0.18	8000	50	22.9	124.6	0.89			153	95	97.90	94.80	0
20	"	0.37	8000	40	41.3	112.4	1.18			156	95	98.19	95.52	0
21	"	0.37	8000	30	25.3	68.8	1.74			157	94	98.70	96.78	0
22	"	0.37	8000	20	11.8	32.0	2.75			158	87	98.75	96.89	0

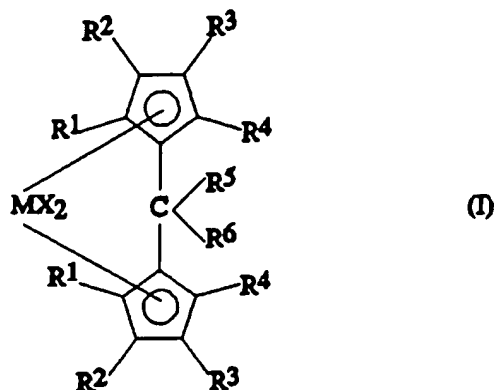
Ex	metallocene	Zr (μmol)	Al/Zr (mol)	T ($^{\circ}\text{C}$)	yield (g)	activity ($\text{Kg}_p/\text{mmol}_Z\text{h}$)	I.V. (dL/g)	Mw/Mn	XSRT (%)	T _m ($^{\circ}\text{C}$)	ΔH_m (J/g)	m (%)	numm (%)	2,1 insertion %
23	$\text{Me}_2\text{C}(\beta\text{-iBu-Ind})_2\text{ZrCl}_2$	0.37	8000	60	41.3	112.4	0.53		0.6	148	97			
24	"	0.37	8000	40	30.0	81.6	1.09		0.5	156	92			
25	"	0.37	8000	20	4.6	12.4	2.97		0.6	159	86			
26	$\text{Me}_2\text{C}(\beta\text{-iBu-H}_4\text{Ind})_2\text{ZrCl}_2$	1.81	3000	70	18.6	10.3	wax							
27	"	1.81	3000	50	19.1	10.5	wax			100	41	94.14	85.79	0
28	$\text{Me}_2\text{C}(\beta\text{-iBu-Cp})_2\text{ZrCl}_2$	2.25	3000	50	34.8	15.5	0.26			153	108	99.77	99.44	0.35
29	"	9.00	3000	20	16.9	1.9	0.53			159	96			
30	$\text{Me}_2\text{C}(\text{2-Me-4-iBu-Cp})_2\text{ZrCl}_2$	0.42	8000	70	58.7	138.8	0.42	2.18	0.4	157	112	99.50	98.74	0.23
31	"	0.42	8000	60	50.7	119.9	0.69	1.95		160	106			
32	"	0.42	8000	50	30.7	72.6	0.89	1.90	0.2	162	106	99.78	99.45	0.16
33	"	0.42	8000	35	10.2	24.2	1.51	2.05		164	96			
34	"	0.42	8000	20	3.9	9.3	2.18		0.2	165	89	99.86	99.65	0.02
35	"	59.24	2000	50	3190	78.5	0.92	2.41		160	115	99.68	99.20	0.14
36	"	122.71	2000	35	3281	24.2	1.7	2.35		162	113	99.74	99.35	0.07

TABLE 2

Ex.	metallocene	Zr (μ mol)	Al/Zr (mol)	T (°C)	yield (g)	activity (K_g pol/mmol $_Z$ h)	I.V. (dL/g)	Mw/Mn	XSRT (%w)	T _m (°C)	ΔH_m (J/g)	1-butene (mol %)
37	$Me_2C(2-Me-4-tBu-Cp)_2ZrCl_2$	0.42	8000	40	22.7	113.7	1.43	1.93	0.2	143	77	5.52
38	$Me_2C(3-tBu-Ind)_2ZrCl_2$	0.37	8000	40	4.77	23.9	1.01	1.88	0.8	133	73	6.98

CLAIMS

1. A metallocene compound of the formula (I):



wherein R^1 , R^2 , R^3 and R^4 , which can be identical or different, are hydrogen atoms or C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl groups which can contain silicon or germanium atoms, R^3 being different from R^2 and from a hydrogen atom, and wherein R^1 and R^2 on the same cyclopentadienyl ring can form a ring having 5 to 8 carbon atoms;

R^5 is a hydrogen atom or a $-CHR^7R^8$ group;

R^6 is a C_6 - C_{20} -aryl radical or a $-CHR^9R^{10}$ group;

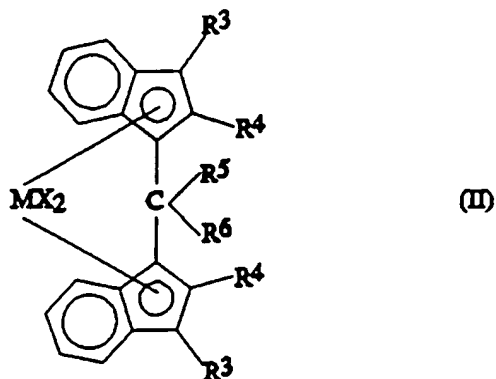
R^5 and R^6 can form a ring having 3 to 8 carbon atoms which can contain hetero atoms;

R^7 , R^8 , R^9 and R^{10} , which can be identical or different, are hydrogen atoms or C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radicals which can contain hetero atoms such as nitrogen, phosphor, oxygen or sulphur, and two R^7 , R^8 , R^9 and R^{10} substituents can form a ring having 3 to 8 carbon atoms which can contain hetero atoms;

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements (new IUPAC version);

the X substituents, which can be identical or different, are hydrogen atoms, halogen atoms or R, OR, SR, NR₂ or PR₂ groups, wherein the R substituents are C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals which can contain silicon or germanium atoms; with the proviso that, when the R¹, R² and R⁴ substituents are hydrogen atoms and the R⁵ and the R⁶ substituents are methyl groups, then the R³ substituents are other than an isopropyl or tertbutyl group.

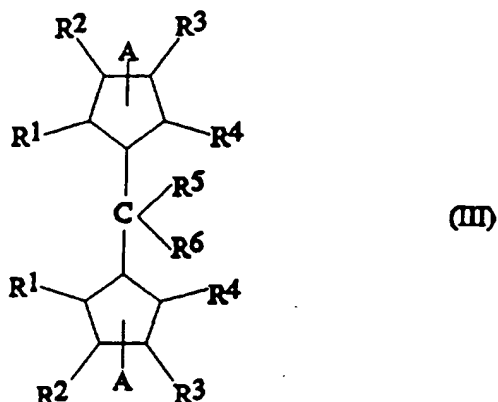
2. The metallocene compound according to claim 1, wherein the transition metal M is selected between titanium, zirconium and hafnium.
3. The metallocene compound according to claim 1 or 2, wherein the X substituents are chlorine atoms or methyl groups.
4. The metallocene compound according to any of claims 1 to 3, wherein the R² substituents are hydrogen atoms.
5. The metallocene compound according to claim 4, wherein the R¹ substituents are different from hydrogen atoms.
6. The metallocene compound according to claim 4 or 5, wherein the R³ substituents are carbon, silicon or germanium atoms substituted with three alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl groups having 1 to 10 carbon atoms.
7. The metallocene compound according to any of claims 4 to 6, wherein the R⁴ substituents are hydrogen atoms.
8. A metallocene compound of the formula (II):



and the corresponding bis-4,5,6,7-tetrahydroindenyl compound, wherein R^3 , R^4 , R^5 , R^6 , M and X are defined as in any of the preceding claims, the six-carbon-atom rings of the indenyl ligands being optionally substituted.

9. The metallocene compound according to claim 8, wherein the R^3 substituents are carbon, silicon or germanium atoms substituted with three alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl groups having 1 to 10 carbon atoms.
10. The metallocene compound according to claim 8 or 9, wherein the R^4 substituents are hydrogen atoms.
11. A process for the preparation of a metallocene compound as claimed in any of claims 1 to 10, comprising the reaction of the corresponding bis-cyclopentadienyl ligands of the formula

(III):



wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are defined as above, and A is a suitable leaving group, with a compound of the formula MX_4 wherein M and X are defined as in any of the preceding claims.

12. A catalyst for the polymerization of olefins, consisting of the product of the reaction between:

- (a) a metallocene compound as claimed in any of claims 1 to 10, and
- (b) an alumoxane or a compound able to form an alkylmetallocene cation.

13. A process for the polymerization of olefins, said process comprising the polymerization reaction of an olefin monomer in the presence of a catalyst as claimed in claim 12.

14. The process for the polymerization of olefins according to claim 13, wherein the olefin monomer is propylene.

15. The process for the polymerization of propylene according to claim 14, wherein propylene is polymerized in the presence of a metallocene compound of the formula (II), wherein the R^3 substituents are carbon, silicon or germanium atoms substituted

with three alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl groups having 1 to 10 carbon atoms, and wherein R^4 , R^5 , R^6 , M and X are defined as above, the R^4 substituents being preferably hydrogen atoms.

16. The process for the polymerization of propylene according to claim 15, wherein the metallocene compound of the formula (II) is selected between:

isopropylidene-bis(3-t-butyl-indenyl)zirconium dichloride,
isopropylidene-bis(3-trimethylsilyl-indenyl)zirconium dichloride, and
isopropylidene-bis(3-trimethylgermyl-indenyl)zirconium dichloride.

17. The process for the polymerization of propylene according to claim 14, wherein propylene is polymerized in the presence of a metallocene compound of the formula (I) in which the R^2 substituents are hydrogen atoms and the R^3 substituents are carbon, silicon or germanium atoms substituted with three alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl groups having 1 to 10 carbon atoms, the R^4 substituents being preferably hydrogen atoms.
18. The process for the polymerization of propylene according to claim 17, wherein in the metallocene compound of the formula (I) the R^1 substituents are different from hydrogen atoms.
19. The process for the polymerization of propylene according to claim 18, which is carried out at a temperature of at least 50°C.
20. The process for the polymerization of propylene according to claim 17, wherein the metallocene compound of the formula (II) is selected between:
isopropylidene-bis(3-t-butyl-cyclopentadienyl)zirconium dichloride, and

isopropylidene-bis(2-methyl-4-*t*-butyl-cyclopentadienyl)zirconium dichloride.

21. A propylene homopolymer having the following characteristics:

- molecular weight distribution (Mw/Mn) lower than 4,
- isotactic (mmmm), as determined by ^{13}C -NMR analyses, pentads higher than 70%,
- no structural units due to regioirregular insertions detectable at the ^{13}C -NMR analysis carried out with a 300 MHz instrument.

22. A propylene homopolymer having the following characteristics:

- molecular weight distribution (Mw/Mn) lower than 4,
- isotactic (m) diads, as determined by ^{13}C -NMR analyses, higher than 99%.

23. A propylene copolymer with 0.1-10% by moles of a C_4 - C_{10} α -olefin comonomer, having the following characteristics:

- isotactic (m) diads, as determined by ^{13}C -NMR analyses, higher than 70%,
- molecular weight distribution (Mw/Mn) lower than 4,
- xylene-soluble fractions lower than 3% by weight.

24. The propylene copolymer according to claim 23, wherein the α -olefin comonomer is 1-butene.

INTERNATIONAL SEARCH REPORT

International Application No

PC1/EP 96/00171

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F17/00 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 516 018 (HOECHST AG) 2 December 1992 see page 12 - page 13; example 18 ---	1-24
Y	EP,A,0 485 821 (HOECHST AG) 20 May 1992 see page 13; example XIII ---	1-24
Y	EP,A,0 485 823 (HOECHST AG) 20 May 1992 see page 11; example XIII ---	1-24
Y	EP,A,0 588 208 (HOECHST AG) 23 March 1994 see page 12; example 15 ---	1-24
Y	EP,A,0 416 566 (HOECHST AG) 13 March 1991 cited in the application see the whole document ---	1-24
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 March 1996

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INTERNATIONAL SEARCH REPORT

International Application No

PC/EP 96/00171

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 629 632 (MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 21 December 1994 see the whole document ---	1-24
P,X	EP,A,0 645 401 (HOECHST AG) 29 March 1995 see page 7, line 19 ---	1-24
P,X	CHEMICAL ABSTRACTS, vol. 123, no. 15, 9 October 1995 Columbus, Ohio, US; abstract no. 199013, URAZOWSKI I ET AL 'syn-[2,2-Bis(3-isopropyl)-.eta.5-cyclopentadienyl)propane]dichlorotitanium' see abstract & ACTA CRYSTALLOGR., SECT. C: CRYST. STRUCT. COMMUN. (ACSCE,01082701);95; VOL.C51 (6); PP.1063-4, RUSSIAN ACADEMY OF SCIENCES;INST. CHEMICAL PHYSICS; CHERNOGOLOVKA; 142432; RUSSIA (RU), -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/00171

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-629632		JP-A- 7196734	01-08-95

EP-A-645401	29-03-95	DE-A- 4333128	30-03-95
		CA-A- 2133181	30-03-95
		FI-A- 944480	30-03-95
		JP-A- 7179512	18-07-95

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 96/00171

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-516018	02-12-92	AU-B- 656968	23-02-95
		AU-B- 1713392	03-12-92
		CA-A- 2069602	28-11-92
		EP-A- 0702030	20-03-96
		JP-A- 5140227	08-06-93
		US-A- 5350817	27-09-94

EP-A-485821	20-05-92	AU-B- 640287	19-08-93
		AU-B- 8776091	14-05-92
		CA-A- 2055218	13-05-92
		JP-A- 6340684	13-12-94
		US-A- 5276208	04-01-94

EP-A-485823	20-05-92	AU-B- 641341	16-09-93
		AU-B- 8775791	14-05-92
		CA-A- 2055219	13-05-92
		DE-D- 59104869	13-04-95
		ES-T- 2071888	01-07-95
		JP-A- 4300887	23-10-92
		US-A- 5145819	08-09-92

EP-A-588208	23-03-94	AU-B- 4626393	17-03-94
		CA-A- 2105914	13-03-94
		FI-A- 933957	13-03-94
		JP-A- 6179776	28-06-94
		ZA-A- 9306696	05-04-94

EP-A-416566	13-03-91	DE-A- 3929693	14-03-91
		AU-B- 625142	02-07-92
		AU-B- 6219090	14-03-91
		CA-A- 2024718	08-03-91
		JP-A- 3100004	25-04-91

EP-A-629632	21-12-94	CA-A- 2125247	08-12-94
		CN-A- 1103405	07-06-95
		JP-A- 7286005	31-10-95
		JP-A- 7149833	13-06-95
		CA-A- 2155016	01-06-95
		EP-A- 0682042	15-11-95
		WO-A- 9514717	01-06-95